07 - 10 September 2009

PROCEEDINGS

# 54. IWK

Internationales Wissenschaftliches Kolloquium
International Scientific Colloquium

# Information Technology and Electrical Engineering - Devices and Systems, Materials and Technologies for the Future

Faculty of Electrical Engineering and Information Technology

Startseite / Index:
http://www.db-thueringen.de/servlets/DocumentServlet?id=14089

TECHNISCHE UNIVERSITÄT
ILMENAU

**Impressum**

Herausgeber: Der Rektor der Technischen Universität Ilmenau
Univ.-Prof. Dr. rer. nat. habil. Dr. h. c. Prof. h. c.
Peter Scharff

Redaktion: Referat Marketing
Andrea Schneider

Fakultät für Elektrotechnik und Informationstechnik
Univ.-Prof. Dr.-Ing. Frank Berger

Redaktionsschluss: 17. August 2009

Technische Realisierung (USB-Flash-Ausgabe):
Institut für Medientechnik an der TU Ilmenau
Dipl.-Ing. Christian Weigel
Dipl.-Ing. Helge Drumm

Technische Realisierung (Online-Ausgabe):
Universitätsbibliothek Ilmenau
ilmedia
Postfach 10 05 65
98684 Ilmenau

Verlag:
Verlag ISLE, Betriebsstätte des ISLE e.V.
Werner-von-Siemens-Str. 16
98693 Ilmenau



ISBN (USB-Flash-Ausgabe): 978-3-938843-45-1
ISBN (Druckausgabe der Kurzfassungen): 978-3-938843-44-4

Startseite / Index:
http://www.db-thueringen.de/servlets/DocumentServlet?id=14089

# ELECTRODEPOSITION OF THIN FE-, CO- AND FECO LAYERS FROM CHOLINE CHLORIDE BASED DEEP EUTECTIC SOLVENTS (DES)

*Sven-Erik Wulf*[a], *Reinhard Böck*[a] *and Christine Jakob*[b]

[a]*fem* - Research Institute Precious Metals and Metals Chemistry, Dep. of Electrochemistry and Electroplating, D-73525 Schwäbisch Gmünd, Germany
[b]Ilmenau University of Technology, Dep. of Electrochemistry and Metal Finishing D-98693 Ilmenau, Germany

## ABSTRACT

The physical and electrochemical properties of choline chloride/urea mixtures containing $CoCl_2$ and $FeCl_3$ were investigated through conductivity, viscosity measurements and cyclo voltammetry. The influence of the temperature and metal content on the conductivity und viscosity was examined. Through electrodeposition experiments of cobalt, iron and iron-cobalt on copper, the dependence of current efficiency, deposition rates and film composition on the temperature and the applied current densities could be demonstrated. In the case of cobalt the temperature limits the applicable current density while the current efficiency could reach 90%. During iron deposition the temperature clearly effects current efficiencies. Additionally, the electrodeposition of FeCo from DES could be demonstrated, while the composition of the received films strongly depends on the electrolyte composition.

***Index Terms—*** electrodeposition, deep eutectic solvent, ionic liquids, iron, cobalt, iron-cobalt

## 1. INTRODUCTION

With the onward going miniaturisation of technical systems in the field of sensor systems, actuating elements and electronic systems [1], new ferromagnetic components are required e.g. for micro motors and micro valves [2] or for hard magnetic recording devices [3]. To achieve improved or new coating systems and also coating properties, which could expand the field of possible applications for electroplating, ionic liquids as a new class of electrolytes for the electrodeposition of metals have received growing attention over the last three decades [4]. Ionic Liquids (IL), also called room temperature molten salts, are compounds of discrete organic cations and inorganic or organic anions, which form by definition a liquid below 100°C. These ILs exhibit some interesting chemical and physical properties, like, e.g. very low vapour pressure, wide electrochemical window and a high ionic conductivity and the absence of water. Due to these properties, ionic liquids exhibit some interesting advantages when they are used as electrolytes for metal deposition compared to water based systems. This includes the electrodeposition of electronegative metals like aluminium, tantalum, niobium, molybdenum and tungsten [5]. It is also possible to coat water sensitive substrates like aluminium or magnesium [6] by using ionic liquids as electrolytes. Additionally many of other metals like palladium [4], nickel [5], cobalt [7, 8], iron [9] and others [10], could be electroplated from ionic liquids. This can offer advantages in comparison with aqueous electrolytes. For instance it is possible to electrodeposit nanocrystalline metal films through direct electroplating from ionic liquids [11]. Unfortunately, a big handicap is that ionic liquids are relatively expensive, because especially for the electrodeposition of electronegative metals like aluminium, they have to be water free. But for less electronegative metals small amounts of water might be tolerable. In 2003 Abbott and co-workers presented a new kind of compound, which consists of a eutectic mixture of choline chloride and different amides [12], which are forming liquids at room temperature. These so called deep eutectic solvents (DES), exhibit many properties of „real“ ionic liquids, but contain small amounts of water. The big advantage of these mixtures is the relatively low price, which makes these mixtures look interesting for the electrodeposition of metals.

## 2. EXPERIMENTAL

The basic electrolyte was made by mixing choline chloride (Fluka, 97%) and urea (Fluka, 99%) in a molar ratio of 1:2. Afterwards, this mixture was processed at 90°C under partial vacuum for 5 hours to remove traces of ammonia and amines. The metal electrolytes for the experiments were prepared by addition of 0.1mol/l and 0.3mol/l anhydrous iron(III) chloride (Alfa Aesar, 98%) and anhydrous cobalt chloride (Alfa Aesar, 99,7%), respectively, and solvating them at 90°C under agitation. The viscosities were measured in dependence of the temperature using a rotating viscosity meter (Fa. Brookfield, DV-E) fitted with a thermostat jacket. The conductivity measurements, also in de-

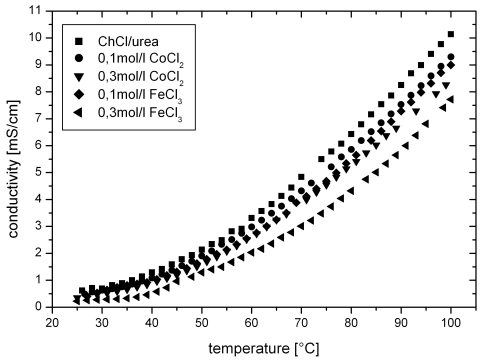


**Fig. 1**. Conductivity of choline chloride/urea mixtures containing 0.1mol/l and 0.3mol/l $CoCl_2$ and $FeCl_3$ in dependence of the temperature

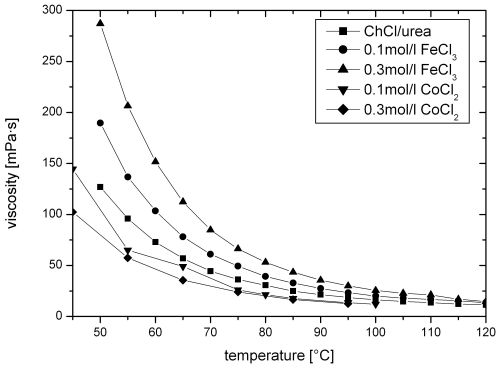


**Fig. 2**. Viscosity of choline chloride/urea mixtures containing 0.1mol/l and 0.3mol/l $CoCl_2$ and $FeCl_3$ in dependence of the temperature

pendence of the temperature, were carried out using a conductivity meter (Cond. 340i, WTW) with a four electrode cell (Tetra Con 325, WTW). Cyclic voltammetry was carried out using a laboratory potentiostat (PST050, Voltalab) with PC control (Voltamaster4, Voltalab). The measurements were performed in a three electrode cell with an electrolyte volume of ca. 40ml. The working electrode was glassy carbon (GC) with an area of 0.07$cm^2$. The counter electrode was a GC-rod (3mm diameter). As reference electrode a self made $Al/Al^{3+}$ electrode was used. This consists of a glass tube, which contains a mixture of aluminium chloride ($AlCl_3$) and 1-butyl-3-methylimidazolium chloride (BmimCl) in a molar ratio of 60:40mol%. In this IL, an aluminium wire (1mm diameter) is immersed. The solution in the glass tube is separated from the electrolyte by a polymer frit. The potential of this $Al/Al^{3+}$ reference electrode against the ferrocene redox couple is -0.32V. Before each experiment the working electrode was polished with a fine emery paper (SiC, 800/2400). The cyclovoltammetry was carried out at 100°C and with a scan rate of 100mV/s. Deposition experiments were carried out in glass beaker containing 100ml of electrolyte, heated by a silicone bath on a heating plate. As a counter electrode a GC-sheet was used. Two kinds of copper substrates were used. For experiments without sample movement copper sheets with an area of 1.5$cm^2$ were used. To be able to apply a defined substrate movement in the case of cobalt deposition, a rotating copper rod (A=1.5$cm^2$, 4mm diameter) was used as substrate. The substrates were polished with emery paper (SiC, 800/2400), rinsed and dried. Before each experiment the substrates were activated in 5%-$H_2SO_4$, rinsed and dried with pressure air before immersion into the electrolyte. The deposition experiments were carried out under constant current conditions. The current was controlled by a potentiostat (PST050, Voltalab). After the deposition the samples were rinsed with deionised water and dried. The layer thickness was determined using energy dispersive X-ray fluorescence spectrometry (EDXRF) (Fischerscope XDAL, Fischer). From these values the cathodic current efficiencies were calculated. To determine surface morphologies and to analyze a high resolution scanning electron microscope (HRSEM) and energy dispersive X-ray spectroscopy (EDS) were used.

## 3. RESULTS

### 3.1. Conductivity and viscosity

Figure 1 shows the influence of temperature and metal content on the conductivity of the solutions. It is observable that the addition of metal chloride to the pure choline chloride/urea mixture leads to decreased conductivities, while this effect seems to be stronger in the case of iron (III) chloride. The decrease of conductivity can be understood by considering the complex formation in this eutectic solvent. For both metals it may be assumed, that chlorocomplexes were formed, probably $[CoCl_4]^{2-}$ and $[FeCl_4]^{-}$, which reduces the amount of small chloride ions which assumedly are the main charge carriers. The general increase of conductivity with temperature could be explained with the higher mobility of the charge carriers at increased temperatures.

Figure 2 show the influence of temperature and metal content on the viscosity. Interestingly, there is a difference between iron and cobalt. The addition of iron leads to a strong increase in viscosity, as formerly reported from the authors [9]. Instead, the addition of cobalt leads to a small decrease in comparison to the pure choline chloride/urea mixture.

### 3.2. Voltammetry

Figure 3 show the cyclovoltammograms of choline chloride/urea mixtures containing 0.3mol/l $FeCl_3$ and $CoCl_2$,

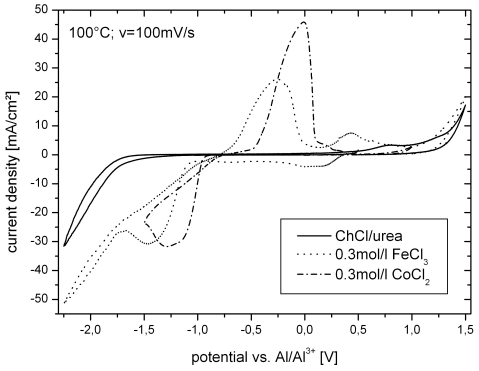


**Fig. 3**. Cyclovoltammogramms of choline chloride/urea mixtures containing 0.3mol/l $CoCl_2$ and $FeCl_3$ at a GC electrode(T=100°C, v=100mV/s

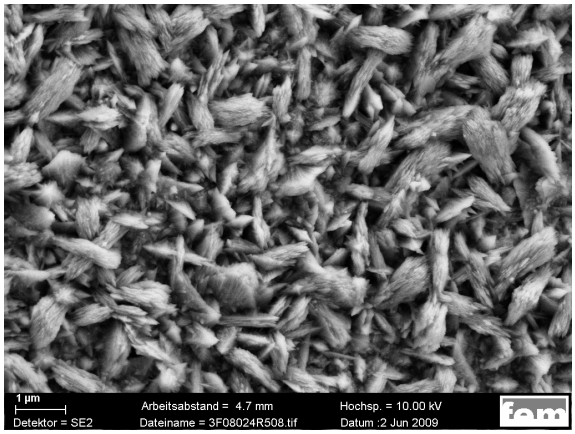


**Fig. 4**. HRSEM image of a cobalt film on copper deposited with 2mA/cm$^2$ at 80°C, with sample movement (800rpm) for 30min. The layer thickness is 1.1$\mu$m.

respectively. In the case of iron, two couples of anodic and cathodic current peaks were observed (see [9]). In comparison, in the cobalt electrolyte only one peak couple is visible. The strong peaks at $E_c$=-1.49V vs. $Al/Al^{3+}$ for iron and $E_c$=-1.29V vs. $Al/Al^{3+}$ in the case of cobalt, correspond to the metal reduction. It is obvious that the reduction of iron needs a higher overpotential then the reduction of cobalt. The peaks at -0.27V vs. $Al/Al^{3+}$ and -0.01V vs. $Al/Al^{3+}$ are the oxidation peaks for the dissolution of the metal. The relatively negative reduction potentials, compared to the standard equilibrium potential of cobalt, indicate, that extra energy is necessary to start the deposition process on the GC electrode [13].

### 3.3. Electrodeposition

*Cobalt deposition* – In table 1 some results of the experiments on the cobalt electrodeposition from a cobalt electrolyte with 0.3mol/l $CoCl_2$ are reported. It could be seen, that the parameters current density and temperature strongly influence the achievable cathodic current efficiencies and deposition rates. Particularly, the applicable current densities are limited through the temperature, mainly because of the increased viscosity and therefore reduced mass transport to the electrode surface. In comparison to former published results from Böck et al. [8] the current efficiencies could be improved from 70%-75% to 74%-90% (in the same current density and temperature range). This is mainly due to the improved mass transport to the electrode surface through rotating the sample, which reduces the diffusion layer in front of the electrode surface. As in the former results reported by the authors in a previous work for the cobalt deposition at 100°C without movement of the sample or electrolyte [8], the application of different current density on moving samples leads also to different surface morphologies. For both temperatures the morphologies were relatively similar. At high current densities the morphologies become more nodular, which goes ahead with a macroscopic change in colour of the deposits. In the first case the films are matt dark grey, in the second they are light grey. As an example

**Table 1**. Current efficiencies and deposition rates for cobalt electrodeposition with sample movement(800rpm) at 80°C and 100°C and different current densities

| T / °C | j=2 mA/cm$^2$ | j=5 mA/cm$^2$ | j=7.5 mA/cm$^2$ | j=10 mA/cm$^2$ |
|---|---|---|---|---|
| 80 | 92% | 78% | 48% | - |
| 80 | 0.04 $\mu$m/min | 0.08 $\mu$m/min | 0.07 $\mu$m/min | - |
| 100 | 90% | 86% | 81% | 74% |
| 100 | 0.04 $\mu$m/min | 0.09 $\mu$m/min | 0.12 $\mu$m/min | 0.15 $\mu$m/min |

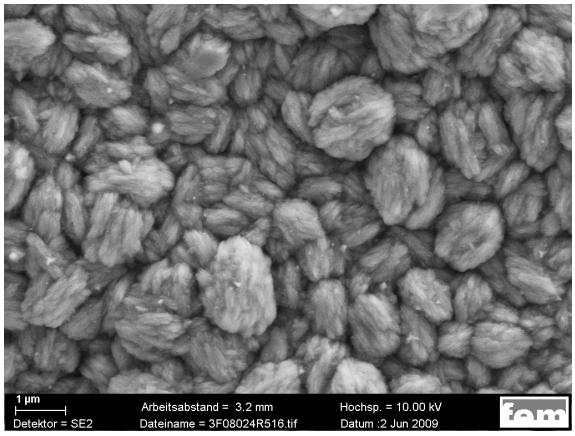


**Fig. 5**. HRSEM image of a cobalt film on copper deposited with 7.5mA/cm$^2$ at 80°C, with sample movement (800rpm) for 30min. The layer thickness is 2.2$\mu$m.

**Table 2**. Current efficiencies and deposition rates for iron electrodeposition at 70°C and 100°C and different current densities

| T / °C | j=2 mA/cm$^2$ | j=5 mA/cm$^2$ | j=7.5 mA/cm$^2$ | j=10 mA/cm$^2$ |
|---|---|---|---|---|
| 70 | 35% | 50% | 40% | 35 |
| 70 | 0.013 $\mu$m/min | 0.037 $\mu$m/min | 0.043 $\mu$m/min | 0.05 |
| 100 | 11% | 13% | 33% | 34% |
| 100 | 0.003 $\mu$m/min | 0.01 $\mu$m/min | 0.037 $\mu$m/min | 0.05 $\mu$m/min |

the surface morphologies of two samples produced at 80°C and two different current densities are presented in figure 4 and 5.

*Iron deposition* – In table 2 results of the deposition experiments are presented. The values for current efficiency and deposition rate at 70°C are new results, while the ones for 100°C are taken from the literature [9]. In both cases the experiments were carried out without sample movement (low hydrodynamic conditions). It is apparent that the deposition rates and current efficiencies at 70°C are higher then at 100°C. On the other hand, the efficiencies and deposition rates are much lower then those which could be achieved from the cobalt chloride solutions. From the cyclovoltammograms presented above, it is visible that for the deposition of iron a higher overpotential is necessary then for the deposition of cobalt. At these higher potentials it might be possible to produce hydrogen at the electrode, because the electrolyte might not be absolute water free. An indication for this is the observation of gas evolution at the cathode, which seems to be stronger at higher current densities and also higher in the case of iron in comparison to cobalt.

*Iron-Cobalt deposition* – In table 3 the influence of the electrolyte composition on the film composition and the current efficiencies is shown. These deposition experiments were carried out at 70°C, with a current density of 2mA/cm$^2$ (30min) under the influence of moderate agitation. It is obvious, that the composition of the electrolyte has a strong impact on the cobalt content in the deposited films. This is also well known from the electrodeposition of FeCo-alloys from aqueous solutions [14]. On the contrary the impact on the current

**Table 3**. Cobalt content and current efficiencies of FeCo-films deposited with 2mA/cm$^2$ for 30min at 70°C and with agitation of the electrolyte

| $CoCl_2$/$FeCl_3$ mol/l | Co % | Efficiency % |
|---|---|---|
| 0.05/0.05 | 81 | 52 |
| 0.05/0.10 | 71 | 48 |
| 0.05/0.20 | 55 | 47 |

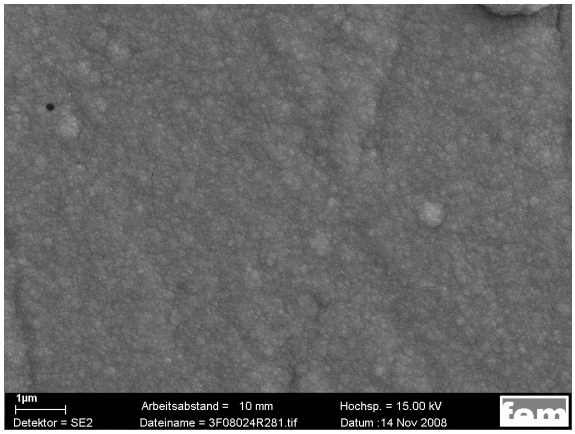


**Fig. 6**. HRSEM image of a FeCo film on copper deposited with 2mA/cm$^2$ for 30min at 70°C (with agitation). The electrolyte contained 0.05mol $CoCl_2$ and 0.05mol/l $FeCl_3$.The layer thickness is 0.6$\mu$m.

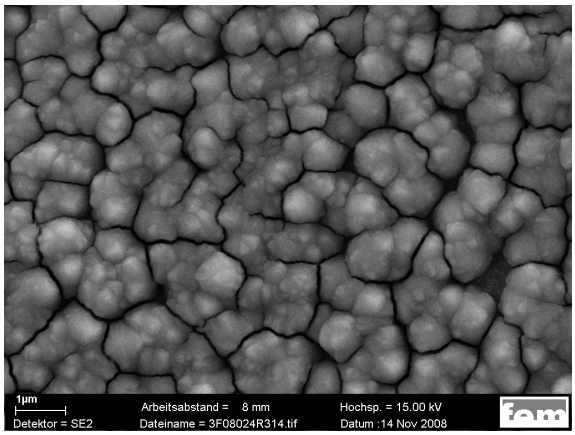


**Fig. 7**. HRSEM image of a FeCo film on copper deposited with 2mA/cm$^2$ for 30min at 70°C (with agitation). The electrolyte contained 0.05mol $CoCl_2$ and 0.2mol/l $FeCl_3$.The layer thickness is 0.5$\mu$m.

efficiencies seems not so strong. The iron content has also a great impact on the surface morphologies, which changed with increased iron content, from a really fine grained microcrystalline structure at low iron contents (see fig. 6), to a nodular shaped structure (see fig. 7). In the second case the thin films also exhibit microcracks.

## 4. SUMMARY

In this study a comparison of physical and electrochemical properties between choline chloride/urea mixtures containing iron (III) chloride and cobalt chloride was presented. The results show, that the electrodeposition of both metals could be influenced by changing temperature, because the physical properties like e.g. conductivity and viscosity are changed significantly through it. In addition these properties also influence the mass transport situation in the discussed electrolyte

systems. Additionally, first results on the electrodeposition of FeCo-films from choline chloride based eutectic mixtures were demonstrated. These results suggest that, through optimizing electrolyte composition and deposition parameters, it should be possible, to produce homogeneous, fine grained FeCo-films from these mixtures. In further investigations it is planned to determine the influence of the structure of the deposits on material properties especially hardness, corrosion resistance and magnetic properties.

## 5. ACKNOWLEDGEMENTS

The authors would like to thank Rita Bretzler and Britta Schöne for carrying out the HRSEM investigations and Dr. Andreas Reisinger (Iolitec) for carrying out the viscosity measurements.

## 6. REFERENCES

[1] N. Holstein, K. Jüttner, M. Küpper, and H. Löwe, "Abscheidung hartmagnetischer schichten aus nichtwässrigen elektrolyten für die mikrosystemtechnik," *Galvanotechnik*, vol. 90, pp. 480–491, 1999.

[2] T. Mache, "Production of micro-valve components for magnetic micro-direct drives," *Galvanotechnik*, vol. 99, pp. 3084–3088, 2008.

[3] D. E. Laughlin, S. Kumar, Y. Peng, and A. G. Roy, "Engineering the microstructure of thin films for perpendicular recording," *IEEE Transactions on Magnetics*, vol. 41, pp. 719–723, 2005.

[4] R. Böck, "Application potentials of ionic liquids based electrolytes in electroplating," *Materialwissenschaft und Werkstofftechnik*, vol. 39, pp. 901–906, 2008.

[5] A. P. Abbott, K. El Ttaib, K. S. Ryder, and E. L. Smith, "Electrodeposition of nickel using eutectic based ionic liquids," *Transactions of the Institute of Metal Finishing*, vol. 86, pp. 234–240, 2008.

[6] A. Bakkar and V. Neubert, "Electrodeposition onto magnesium in air and water stable ionic liquids: From corrosion to successful plating," *Electrochemistry Communications*, vol. 9, pp. 2428–2435, 2007.

[7] S. Schaltin, P. Nockemann, B. Thijs, K. Binnemans, and J. Fransaer, "Influence of the anion on the electrodeposition of cobalt from imidazolium ionic liquids," *Electrochemical and Solid-State Letters*, vol. 10, pp. D104–D107, 2007.

[8] R. Böck and S.-E. Wulf, "Electrodeposition of cobalt from deep eutectic solutions," *Galvanotechnik*, vol. 100, pp. 264–269, 2009.

[9] R. Böck and S.-E. Wulf, "Electrodeposition of iron films from an ionic liquid (chcl/urea/fecl3-deep eutectic mixtures)," *Transactions of the Institute of Metal Finishing*, vol. 87, pp. 28–32, 2009.

[10] A. P. Abbott, K. S. Ryder, and U. König, "Electrofinishing of metals using eutectic based ionic liquids," *Transactions of the Institute of Metal Finishing*, vol. 86, pp. 196–204, 2008.

[11] N. Natter and R. Hempelmann, "Nanocrystalline metals prepared by electrodeposition," *Zeitschrift für physikalische Chemie*, vol. 222, pp. 319–354, 2008.

[12] A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed, and V. Tambyrajah, "Novel solvent properties of choline chloride/urea mixtures," *Chemical Communications*, pp. 70–71, 2003.

[13] A. B. Soto, E. M. Acre, M. Palomar-Pardavé, and I. González, "Electrochemical nucleation of cobalt onto glassy carbon electrode from ammonium chloride solutions," *Electrochimica Acta*, vol. 41, pp. 2647–2655, 1996.

[14] N. Mattoso, V. Fernandes, M. Abbate, W. H. Schreiner, and D. H. Mosca, "Structural and chemical characterization of fe-co alloys prepared by electrodeposition," *Electrochemical and Solid-State Letters*, vol. 4, pp. C20–C22, 2001.